Proc. Nat. Acad. Sci. USA
Vol. 68, No. 12, pp. 3216–3218, December 1971

Evidence for Hydrogen Abstraction by Classical Radicals in the Norbornenyl–Nortricyclyl System*

(free radical rearrangement/symmetrical intermediates/mechanism)

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ABSTRACT **Studies of product compositions and deuterium-label rearrangements at various concentrations of tri-*n*-butyltin hydride in the reductions of *exo*- and *endo*-5-bromonorbornene and 2-bromonortricyclene to mixtures of norbornene and nortricyclene lead to three main conclusions: (*i*) at least two radical intermediates contribute to product formation; (*ii*) each intermediate yields predominantly (80% or more) one product; and (*iii*) nortricyclene is predominantly derived from a symmetrical intermediate. This constitutes strong evidence for hydrogen abstraction by classical (i.e., single-product) norbornenyl and nortricyclyl radicals. It is argued that the norbornenyl–nortricyclyl system is exceptionally well suited for the generation of a nonclassical (dual-product) radical; hence, the existence of a nonclassical radical in any other system is rather unlikely.**

Many rate-enhancement and product-composition studies have implicated nonclassical carbonium ions as reaction intermediates (1). In contrast, no definite evidence has been reported for a nonclassical radical, that is, a σ radical in which the unpaired electron is sufficiently delocalized that reaction can occur at more than one center or with the stereospecificity characteristic of some nonclassical cations†. Thus, only small rate enhancements have been reported in reactions in which free-radicals are formed (2), and formation of products from classical radical intermediates can account for the results of extensive studies of product composition (3). Indeed, in most cases, the exclusive intermediacy of a single delocalized radical can be ruled out (3). Nevertheless, no available evidence excludes product formation partly from a nonclassical radical. For example, Kuivila's work on the norbornenyl–nortricyclyl system (3*a*) clearly shows the presence of at least two radical intermediates, but does not reveal their precise nature.

We report here evidence from product-composition and isotopic-labeling studies that the radical intermediates in the norbornenyl–nortricyclyl system are, in fact, the classical (i.e., single-product) norbornenyl and nortricyclyl radicals (Fig. 1). This is a significant finding, because the norbornenyl–nortricyclyl system seems exceptionally well suited for the generation of a nonclassical radical. In this case, (*a*) a strong driving force for formation of a nonclassical ion is exhibited in carbonium-ion reactions (4), (*b*) the geometrical requirement for effective homoallylic participation is built in (5), and (*c*) the classical radicals may be expected to have closely similar geometries and energies‡. For these reasons, the conclusion that the radicals in this system are classical indicates that the existence of nonclassical radicals in other systems is rather unlikely.

Radical reduction (6) of *endo*-5-bromonorbornene (*endo*-I), *exo*-5-bromonorbornene (*exo*-I), and 2-bromonortricyclene (II) by tri-*n*-butyltin hydride in toluene produces norbornene (V) and nortricyclene (VI) as the only major hydrocarbon products (3*a*), in 90–100% yield, either thermally (0 to 25°C) or photolytically (−10 to 22°C)§. Some results for photolytically initiated reductions at −10°C are shown in Fig. 2.

With both *endo*-I and II, the relative amount of the unrearranged hydrocarbon increases linearly with tin hydride concentration. At least two product-forming intermediates are required to account for this result; for simplicity and economy, the classical norbornenyl (III) and nortricyclyl radicals (IV) (Fig. 1) are attractive candidates.

The steady-state hypothesis (7) with the mechanism of Fig. 1 yields for the ratio of V to VI from reduction of *exo*- or *endo*-I:

$$[V]/[VI] = k_a k_2/k_1 k_b + (k_a/k_1)[Bu_3SnH] = A + B[Bu_3SnH]. \quad (1)$$

For reduction of II, this ratio is given by

$$[V]/[VI] = \{1/A + B/A[Bu_3SnH]\}^{-1}, \quad (2)$$

and this should be predictable from product ratios observed with I. The line to the open squares in Fig. 2 has been calculated from Eq. 2, by the use of the values $A = 1.26$ and $B = 0.12$ M^{-1} from the results for *endo*-I. Although there is a systematic deviation¶, the anticipated reciprocal inter-

* Contribution no. 4336 from the Gates and Crellin Laboratories of Chemistry.

† The distribution of the unpaired electron may be the best measure of nonclassical character. However, we use here an operational definition based on reactivity. A stereospecificity argument for a nonclassical radical, Warkentin, J., and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968), has been shown to be quantitatively, and probably qualitatively, incorrect; Cristol, S. J., and A. L. Noreen, *J. Amer. Chem. Soc.*, **91**, 3969 (1969); Russell, G. A., and G. W. Holland, *J. Amer. Chem. Soc.*, **91**, 3968 (1969).

‡ Thus, the free energies of norbornene and nortricyclene differ by only 1 kcal/mol at 100°C [Schleyer, P. v. R., *J. Amer. Chem. Soc.*, **80**, 1700 (1958)], and in each case conversion to the radical requires the breaking of a secondary C–H bond.

§ Samples were degassed and, for the photolytic reaction, were irradiated with a Hanovia 450-W high-pressure mercury lamp for the minimal periods necessary for essentially complete reaction of the bromide.

¶ The systematic error (mostly in the predicted intercept) may arise from competing photo-initiated hydrostannation of norbornene. The intercept relationship seems to be more closely obeyed in thermal reactions.

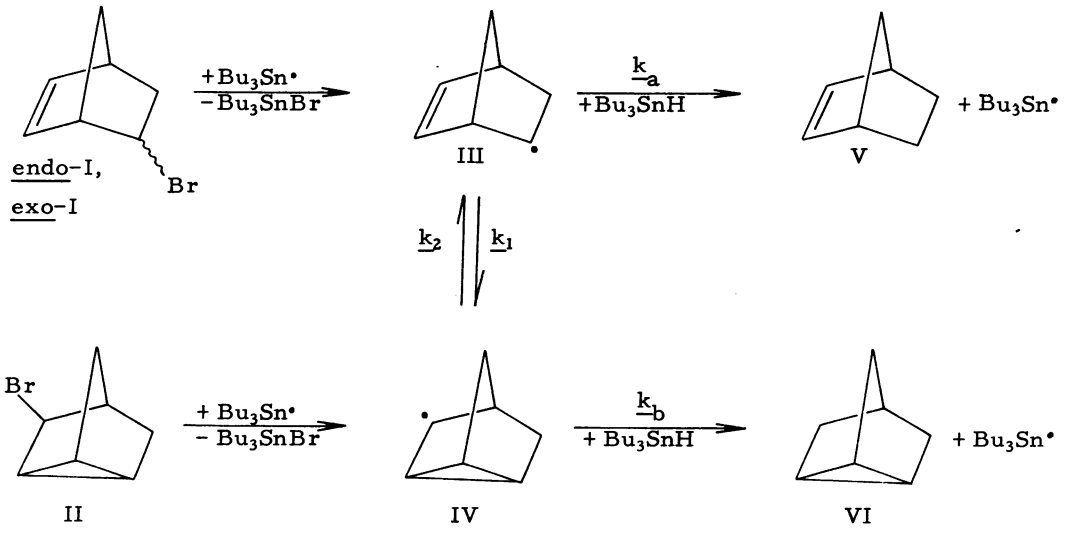

FIG. 1. Mechanism for reduction of I and II by tri-*n*-butyltin hydride, with the assumption of classical radical intermediates.

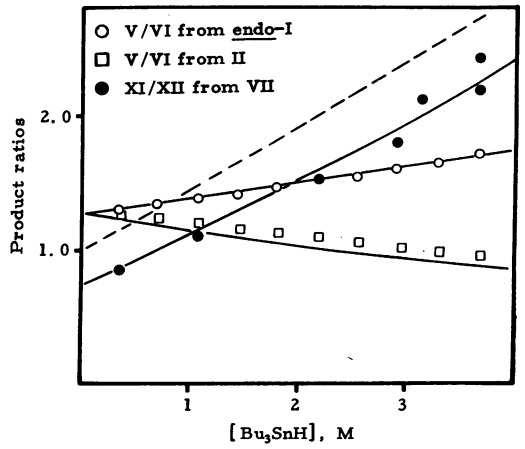

FIG. 2 Product ratios as a function of tri-*n*-butyltin hydride concentration in photolytically initiated reductions at −10°C. The *dashed line* is calculated from Eq. 4, by the use of the values $A = 1.26$ and $B = 0.12\ M^{-1}$. The *solid line* through the points ● is calculated from Eq. 3, with these values of A and B and allowance for secondary deuterium isotope effects, as explained in the text.

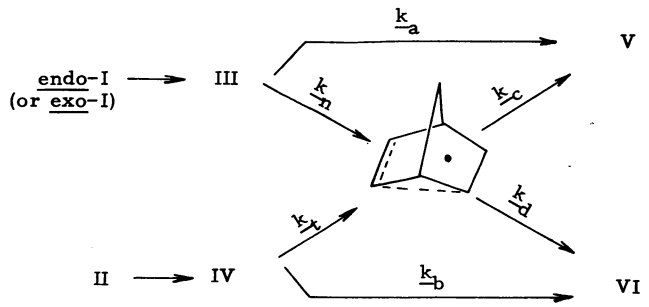

FIG. 3. Mechanism for reduction of bromides I and II, with irreversible formation of an unsymmetrical nonclassical radical.

relationship of slopes and intercepts is reasonably well satisfied. Similar results have been obtained at other temperatures, in thermally initiated reductions, and with the *exo*-bromide.

If $k_a/k_n = k_b/k_t$, the mechanism shown in Fig. 3 also conforms to Eqs. 1 and 2 but with different definitions of A and B. To differentiate these possibilities, we studied the reduction of deuterium-labeled bromonorbornene (VII). Experimental ratios of rearranged (XII) and unrearranged (XI) norbornene-d_3[‖] are shown in Fig. 2 and the classical-radical mechanism is elaborated in Fig. 4. The pairs of carbon atoms, interchanged when norbornenyl-d_3 radicals VIII and X are interconverted, are indistinguishable (apart from the deuterium label) in the nortricyclyl-d_3 radical IX. Because IX is the precursor of XIII, the efficiency of the trapping of VIII to X is directly related to that of VIII relative to IX (or III relative to IV) *in the classical-radical mechanism*. A mechanism in which XIII is to any extent derived from an *asymmetrical* intermediate predicts *less* formation of XII for a given concentration of tin hydride, and, in the limiting case (Fig. 3), *no* XII at all.

For classical radicals, the ratio XI to XII is given by:

$$[XI]/[XII] = (k_a^u k_1^r k_2^u)/(k_a^r k_1^u k_2^r) + \{(2k_a^u k_1^r k_b')/(k_a^r k_1^u k_2^r) + [k_a^u(k_2^u + k_2^r)]/(k_1^u k_2^r)\}[Bu_3SnH] + (2k_a^u k_b')/(k_1^u k_2^r)[Bu_3SnH]^2. \quad (3)$$

If secondary deuterium isotope effects are neglected, Eq. 3 reduces to the form

$$[XI]/[XII] = 1 + 2B(1 + 1/A)[Bu_3SnH] + 2B^2/A[Bu_3SnH]^2. \quad (4)$$

The experimental ratios actually correspond to about 25% *more* XII than is predicted by Eq. 4 with $A = 1.26$ and $B = 0.12\ M^{-1}$ (the dashed line in Fig. 2). This difference is consistent with expected isotope effects on the equilibrium

‖ Assay of cyclopentadiene and cyclopentadiene-d_3 from retro Diels-Alder fragmentation in the mass spectrometer was used to infer the composition of isotopically mixed norbornene-d_3. Spectra for norbornene and norbornene-d_4 give no evidence for an isotope effect on the efficiency of fragmentation.

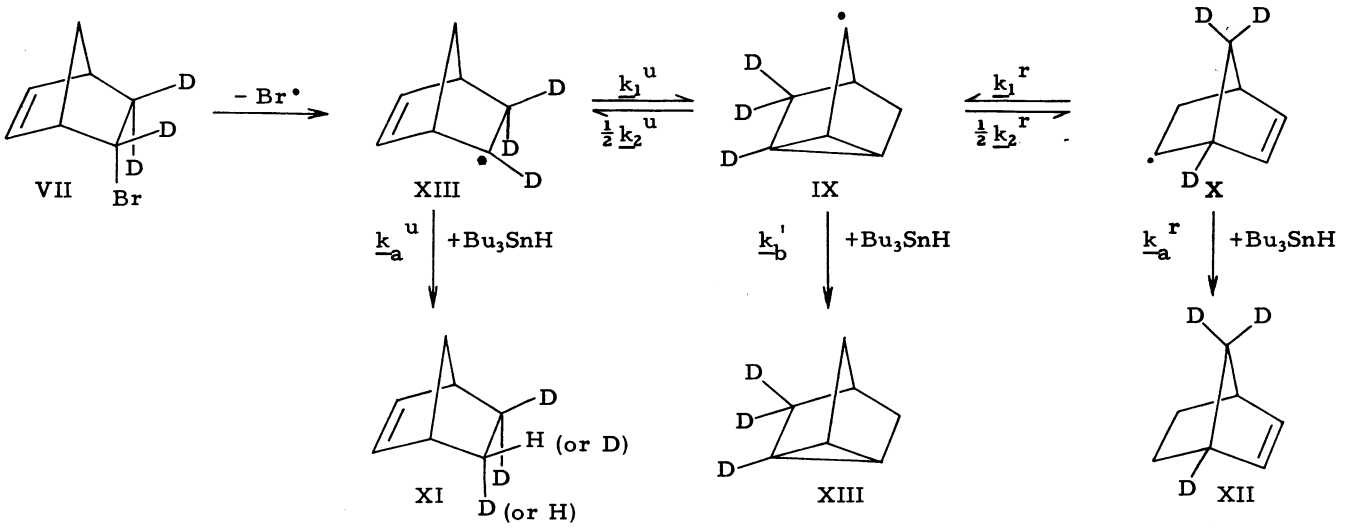

FIG. 4. The classical-radical mechanism for reduction of *endo*-5-bromonorbornene-5,6,6-d_3. Note that, apart from the deuterium label, IX has a plane of symmetry.

between VIII and X. Thus, rearranged radical X should be favored over VIII at −10°C by 15–20% because the trigonal α-deuterated carbon in VIII is tetrahedral in X (8), and by an additional 5–10% because the CD_2 group is adjacent to the radical center in VIII (9), or 20–30% overall**.

For nonzero hydride concentrations, the product ratios calculated from Eq. 3 depend slightly on the manner in which the isotope effect is partitioned among the individual reaction steps. The specification $k_1^u = 1.10\ k_1$, $k_1^r = 0.95\ k_1$, $k_2^u = 0.90\ k_2$, $k_2^r = 1.05\ k_2$ yields the solid line in Fig. 2. Clearly, the classical-radical mechanism accounts for the data and the nonclassical-radical mechanism of Fig. 3 does not.

Alternative mechanisms in which (*i*) the "norbornenyl" radical is nonclassical and gives nortricyclene and norbornene in a ratio of α, or (*ii*) the "nortricyclyl" radical is nonclassical and gives norbornene and nortricyclene in a ratio of β cannot be excluded. However, we can show that α and β must be less than 0.2.

No conclusions can be drawn about the precise distribution of the unpaired electron in either radical. Electron spin resonance studies of the kind recently reported for cyclopropylcarbinyl and allylcarbinyl radicals (10) should give direct information on this point, but would offer no test of the possible consequence of delocalization of the unpaired electron. These different approaches to determination of nonclassical character thus complement one another.

This work was supported by the National Science Foundation

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**Isotope effects on k_a^u and k_a^r will also influence the product ratios, but these effects could well be quite small. That there is little structural reorganization in the transition states for these highly exothermic processes‡ is evidenced by a primary isotope effect k_H/k_D of only about 2 for hydrogen abstraction from Bu_3SnH and Bu_3SnD.

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